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(54) **Title**: COATED NANOPARTICLES AND METHODS FOR THEIR PRODUCTION

(57) **Abstract**: Disclosed herein is a method of electrochemically coating nanoparticles, the method comprising (i) providing a working electrode, a counter electrode, and a liquid carrier medium in contact with the working electrode, the liquid carrier medium comprising: (a) the nanoparticles, wherein the nanoparticles comprise a first material; (b) ions of a metal dissolved in the liquid carrier medium; (ii) applying a potential between the working electrode and the counter electrode, such that, at the working electrode, the ions of the metal are reduced and there is a bulk deposition of the elemental metal onto the nanoparticles. Nanoparticles made in accordance with this method are also described. An apparatus for carrying out the method is also described.

Coated nanoparticles and methods for their production

Field of the Invention

The present invention relates to coated nanoparticles and a method for their production, particularly using an electrodeposition technique. The method allows bulk deposition of a metal onto a nanoparticle.

Background to the Invention

Metal nanoparticles, for example silver nanoparticles, have interesting magnetic, optical and electrical properties, which has lead to their use within many fields, including optics, electronics, catalysis, sensors and pharmaceuticals. Core-shell nanoparticles have also been researched extensively, since the differing properties of the materials of the core and shell can be tailored to meet different requirements. There are many available techniques for producing core-shell nanoparticles having a metal core and a non-metal shell, and vice versa. However, there are few viable techniques for producing core-shell particles where both the core and shell are elemental metals. One example of producing core-shell nanoparticles having a metallic core and a metallic shell is described in WO 2009/156990, which is incorporated here by reference in its entirety. In this application, nanoparticles having a copper core and a silver shell are produced by adding silver nitrate to a dispersion of copper nanoparticles, as described in Example 6 of this document. The silver ions are reduced by copper atoms on the surface of the nanoparticles, resulting in a layer of elemental silver on the nanoparticles, with the copper atoms themselves being oxidised. As will be appreciated, it is difficult to monitor the progress of this reaction as it happens, and the outcome of the method can only generally be determined after the nanoparticles have been produced.

It would be desirable to provide a method that is an alternative to or an improvement upon at least one method of the prior art. In particular, it would desirable to provide a method that can produce metal core-metal shell nanoparticles that, for example, avoids having to oxidise the metal core, and/or that can be monitored during production of the core-shell nanoparticles, such that the production of nanoparticles can be finely controlled. It would be desirable to provide a method that allows bulk deposition of a metal onto a nanoparticle.

Summary of the Invention

In a first aspect, the present invention provides a method of electrochemically coating nanoparticles, the method comprising:

(i) providing a working electrode, a counter electrode, and a liquid carrier medium in contact with the working electrode, the liquid carrier medium comprising:

(a) the nanoparticles, wherein the nanoparticles comprise a first material;

(b) ions of a metal dissolved in the liquid carrier medium;

(ii) applying a potential between the working electrode and the counter electrode, such that, at the working electrode, the ions of the metal are reduced and there is a bulk deposition of the elemental metal onto the nanoparticles. The elemental metal is the metal of the ions in solution in elemental form.

In a second aspect, the present invention provides an apparatus for carrying out the method of the first aspect, the apparatus comprising:

a working electrode, a counter electrode, and a liquid carrier medium in contact with the working electrode, the liquid carrier medium comprising:

(a) the nanoparticles, wherein the nanoparticles comprise a first material;

(b) ions of a metal dissolved in the liquid carrier medium;

wherein a potential between the working electrode and the counter electrode can be applied, such that, at the working electrode, the ions of the metal can be reduced and there is a bulk deposition of the elemental metal onto the nanoparticles.

In a third aspect, the present invention provides a coated nanoparticle producible in accordance with the method described in the first aspect.

In a fourth aspect, the present invention provides a nanoparticle having a core comprising a first elemental metal and an electrochemically-deposited coating of a second elemental metal on the core, wherein the coating is in the form of a bulk deposit

of the second elemental metal. The nanoparticle of the fourth aspect may be producible in accordance with the method of the first aspect.

The present inventors have found that they can produce coated nanoparticles by an electrochemical method, including core-shell metal nanoparticles. The electrochemical nature of the deposition is such that the coating on the nanoparticles can be controlled, and such that a bulk deposition of the metal occurs. The process can also be controlled such that substantially only the nanoparticles are coated, not the working electrode.

Brief Description of the Figures

Figure 1 shows a comparative voltammogram of Cadmium deposition on a bare glassy carbon electrode (dotted lines, Example 1) and on a AgNP-modified glassy carbon electrode (solid lines, Example 2). (a) sets forth the full voltammograms, and (b) the underpotential deposition region.

Figure 2 shows (a) a typical impact transient at -0.55V for a glassy carbon microelectrode (of radius 11 μm) which has been placed in a degassed solution of 1 mM $CdCl_2$ and 0.1M KCl, also to which solution an aliquot of dispersed AgNPs has been added and agitated by bubbling with N_2 (Example 3); and (b) a histogram showing the number of impacts in terms of layer coverage of an average AgNP.

Figure 3 shows (a) a potential step-sweep experiment of a glassy carbon electrode (of radius 11μm) in 1mM $CdCl_2$ and 0.10M NaCl (Example 5) in which the potential was held at -0.74V (vs Ag/AgCl) and scanned positive at 20 mV s^{-1}; and (b) an enlargement of the "transient" region after noise reduction to confirm no spikes.

Figure 4 shows similar information to Figure 3, except that, in this example, 9×10^{12} particles dm^{-3} of AgNPs was also present (Example 6).

Figure 5 shows (a) a potential step-sweep experiment of a glassy carbon electrode (of radius 11μm) in 1mM $CdCl_2$ and 0.10M NaCl (Example 7), in which the potential was held at -0.73V (vs Ag/AgCl) and scanned positive at 20 mV s^{-1}; and (b) an enlargement of the "transient" region after noise reduction showing spikes.

Figure 6 shows a histogram of the number of impacts in terms of layer coverage of an average AgNP of Example 7. It sets forth the distribution of nanoparticle coverages, confirming that multilayers of Cd are deposited onto the AgNPs during collision.

Detailed Description

The present invention provides the first to fourth aspects described above. Optional and preferred features of the various aspects are described below. Unless otherwise stated, any optional or preferred feature may be combined with any other optional or preferred feature, and with any of the aspects of the invention mentioned herein.

The nanoparticles, in step (i) of the method, may be particles having a diameter of from 1 to 500 nm, optionally from 1 to 200 nm, optionally from 10 to 90 nm, optionally from 20 to 80 nm, optionally from 30 to 70 nm. The liquid carrier medium, in step (i), may comprise nanoparticles having a mean diameter of from 1 to 500 nm, optionally from 1 to 200 nm, optionally from 10 to 90 nm, optionally from 20 to 80 nm, optionally from 30 to 70 nm. The diameter of a nanoparticle can be determined by scanning electron microscope (SEM) imaging, as would be appreciated by the skilled person. The nanoparticle can be any suitable shape, including spherical, and elongated, for example a rod-shaped nanoparticle. If a nanoparticle is non-spherical, the diameter of the nanoparticle as measured herein will be the smallest diameter across the particle. The mean diameter of nanoparticles in the liquid carrier medium can be measured using SEM imaging of a sample of the nanoparticles, and calculating the number average (i.e. mean) diameter for 100 nanoparticles or more, optionally 200 nanoparticles or more, optionally 300 nanoparticles or more.

The nanoparticles, in step (i), may comprise, consist essentially of, or consist of, a first material. If a particle consists essentially of the first material, this indicates that preferably the particle comprises at least 95 % by weight of the first material, preferably 98 % by weight, preferably 99 % by weight, of the first material. Preferably, the first material is an electrically-conducting material. The first material may be selected from a metal, a semi-metal, and a semi-conductor. Preferably, the first material comprises a metal, preferably in elemental form, which is preferably a different type of metal from the metal of the metal ions in solution. The metal of the first material may be any suitable metal, including, but not limited to, a metal selected from any of groups 3 to 14 of the periodic table. The metal of the first material may be selected from a transition

metal of any of groups 3 to 12 of the periodic table. Optionally, the first material comprises a metal selected from a group 11 of the periodic table. Optionally, the first material comprises a metal in elemental form selected from copper, silver, gold, ruthenium, osmium, rhodium, iridium, palladium and platinum. Preferably, the first material comprises a metal in elemental form selected from silver and gold.

In an embodiment, the nanoparticles are adsorbed on the working electrode and/or dispersed in liquid carrier medium. Preferably, the nanoparticles are dispersed in the carrier medium. Preferably, in step (i), the particles are dispersed in the liquid carrier medium, e.g. by addition to the liquid carrier medium and agitation of the liquid carrier medium (e.g. by ultrasound), and step (ii) is initiated less than 20 minutes after the particles are dispersed in the liquid carrier medium, optionally 15 minutes or less, optionally 10 minutes or less, optionally 5 minutes or less, optionally 2 minutes or less, after the particles are dispersed in the liquid carrier medium.

Optionally, the first material is or comprises a first metal, which is in elemental form, and the metal of the ions in solution is a second metal, the first and second metal being different to one another.

Optionally, the first and second metals are each independently selected from the transition metals, but are different from one another.

The first metal may be a metal higher up or lower down in the electrochemical series than the second metal. Optionally, the first metal is a metal higher up in the electrochemical series than the second metal. In other words, optionally, the first metal is less strongly reducing (has a more positive value for its standard reduction electrode potential) than the second metal. The electrochemical series is known to the skilled person, and is found in many text books, for example as described on page 343 of Physical Chemistry, authored by P. W Atkins, 5th Edition, which is incorporated herein by reference in its entirety.

Optionally, the ions of a metal dissolved in the liquid carrier medium are ions of a metal selected from any one of groups 3 to 13 of the periodic table. Optionally, the ions of a metal dissolved in the liquid carrier medium are ions of a metal selected from group 12 and 13 of the periodic table, including, but not limited to, zinc, cadmium, mercury, indium and thallium. Optionally, the ions of a metal dissolved in the liquid carrier

medium are ions of a transition metal selected from any one of groups 3 to 12 of the periodic table.

Optionally, the ions of the metal dissolved in the liquid carrier medium are ions of a transition metal other than silver, and the first material comprises or is silver. Optionally, the ions of the metal dissolved in the liquid carrier medium are ions of cadmium and the first material comprises or is silver.

"Bulk deposition" and "bulk deposit" are terms known to those skilled in the art. A bulk deposit of a metal onto a substrate (e.g. a nanoparticle) is understood in the art to mean a deposit of more than a monolayer of atoms of the metal onto the substrate (e.g. nanoparticle). Likewise, the bulk deposition in the method of the first aspect results in a plurality of layers of atoms of the elemental metal on the nanoparticle. The bulk deposition of the elemental metal on the particles may result in a partial or complete coating of the elemental metal on the surface of the nanoparticle.

The particle density of the nanoparticles in the liquid carrier medium may be at any suitable density that allows deposition on the nanoparticles of the metal from the metal ions in the liquid carrier medium. The particle density of the nanoparticles in the liquid carrier medium may be at least 1×10^{6} particles dm^{-3} of the liquid carrier medium, optionally at least 1×10^{8} particles dm^{-3} of the liquid carrier medium, optionally at least 1×10^{10} particles dm^{-3} of the liquid carrier medium, optionally at least 1×10^{11} particles dm^{-3} of the liquid carrier medium. The particle density of the nanoparticles in the liquid carrier medium may be from 1×10^{10} particles dm^{-3} of the liquid carrier medium to 1×10^{15} particles dm^{-3} of the liquid carrier medium, optionally from 1×10^{12} particles dm^{-3} of the liquid carrier medium to 1×10^{14} particles dm^{-3} of the liquid carrier medium, optionally 5×10^{12} particles dm^{-3} of the liquid carrier medium to 5×10^{13} particles dm^{-3} of the liquid carrier medium. The particle density of nanoparticles can be measured using any known technique. In one embodiment, the particle density of metal nanoparticles in the liquid carrier medium is measured is follows:

1. Disperse a sample of nanoparticles suspended in the liquid carrier medium (e.g. using ultrasound) and deposit an aliquot (e.g. 20 μL) onto a clean, dry glassy carbon (GC) electrode (radius typically 1-3mm). The liquid of the liquid carrier medium is then allowed to evaporate, to form a nanoparticle-modified GC electrode.

2. Place the nanoparticle-modified GC electrode into an electrochemical cell containing a suitable counter and reference electrode and electrolyte solution. Run an oxidative scan, and record the stripping voltammogram of the nanoparticles being exhaustively oxidised from the surface to become metal ions.

3. By integration of the stripping peak, the number of metal atoms present on the GC electrode surface can be determined from Faraday's Law. Knowing the mean nanoparticle size and density of the nanoparticles, we can convert the number of atoms of metal into a number of nanoparticles. Thus, the number of nanoparticles in the original aliquot (e.g. 20μL) can be found, from which the nanoparticles in a dm^3 of the liquid carrier medium can be calculated.

The ions of the metal dissolved in the liquid carrier medium may be at any suitable concentration to allow deposition of the elemental form of this metal on to the nanoparticles. The ions of the metal may have a concentration in the liquid carrier medium, before step (ii) in the method, of at least 0.01 mM, optionally at least 0.1 mM, optionally at least 0.5 mM. The ions of the metal may have a concentration in the liquid carrier medium, before step (ii) in the method, of from 0.01 mM to 100 mM, optionally from 0.1 mM to 10 mM, optionally from 0.5 mM to 5 mM, optionally from 0.5 mM to 3 mM.

The liquid carrier medium will comprise counter ions for the dissolved ions of the metal. These counter ions may be selected from any suitable counter ions. The counter ions preferably are selected such that they will not themselves be oxidised or reduced under the conditions at which the method is carried out. The counter ions are preferably selected such that a compound of the metal ions and the counter ions will dissolve in the liquid carrier medium, for example such that the metal ions can dissolve at the concentrations mentioned above. The counter ions may, for example, be selected from the halides, including, but not limited to, chlorides, bromides and iodides.

The liquid carrier medium may be any suitable medium. Preferably, the liquid carrier medium comprises, consists essentially of, or consists of (excluding any dissolved solutes and suspended nanoparticles), water. If the carrier medium consists essentially of water, preferably the liquid carrier medium (excluding any dissolved solutes and suspended nanoparticles) comprises at least 98% by weight water,

preferably at least 99% by weight water, preferably at least 99.5% by weight water. The water, before the addition of the metal ions, counter ions and the nanoparticles, may have a resistivity of at least 18 MΩ.cm, preferably at least 18.2 MΩ.cm. Preferably the liquid carrier medium is degassed before the addition of the metal ions, any counter ions and the nanoparticles. The liquid carrier medium may be degassed using any suitable technique, for example degassing using N_2 under an atmosphere of N_2.

The nanoparticles may be dispersed in the liquid carrier medium using any suitable technique. In an embodiment, the nanoparticles are added to the liquid carrier medium and then dispersed in the liquid carrier medium using ultrasound, optionally stirring or otherwise agitating the liquid carrier medium as required.

The working electrode may comprise any suitable material. Preferably, the surface of the working electrode comprises an inert material, such that it is not itself oxidised or reduced under the conditions at which the method is carried out. Suitable electrodes are available to the skilled person. The working electrode may have a surface comprising a metal or carbon. Optionally, the whole of the electrode comprises a metal or carbon. The working electrode may comprise a metal selected from gold, silver and platinum. The working electrode may comprise a carbon-containing material, which may be selected from edge plane pyrolytic graphite, basal plane pyrolytic graphite, glassy carbon, boron doped diamond, highly ordered pyrolytic graphite, carbon powder and carbon nanotubes. In a preferred embodiment, the working electrode is a glassy carbon electrode.

The counter electrode may be made of any suitable material, for example a metal or carbon. If the counter electrode is in contact with the liquid carrier medium, preferably the material of the counter electrode is selected such that it is not itself oxidised or reduced under the conditions at which the method is carried out. The counter electrode may comprise a metal selected from gold, silver and platinum. The counter electrode may comprise a carbon-containing material, which may be selected from edge plane pyrolytic graphite, basal plane pyrolytic graphite, a glassy carbon, boron doped diamond, highly ordered pyrolytic graphite, carbon powder and carbon nanotubes. In a preferred embodiment, the counter electrode is a graphite electrode.

In a preferred embodiment, both the working electrode and the counter electrode are carbon-containing electrodes.

A reference electrode, for example an Ag/AgCl reference electrode or a saturated calomel reference electrode, may be connected to the working and/or counter electrodes as is known in the art. The working electrode, the counter electrode and the reference electrode may be controlled by a potentiostat, as is known by the skilled person.

A means for applying a potential is electrically connected to the working and counter electrodes. The means for applying a potential can be any suitable means, for example a potentiostat, as mentioned above.

Preferably, the potential applied to the working electrode is more than, i.e. a value more positive than, the potential at which the deposition of the elemental metal occurs on the working electrode in the absence of the nanoparticles, but otherwise the conditions being the same as the method. "The potential at which the deposition of the elemental metal occurs on the working electrode in the absence of the nanoparticles" can be determined in a cyclic voltamogram by the single cathodic deposition peak in the sweep from the most positive potential to the most negative potential, using a sweep rate of 100 mVs^{-1} or less, e.g. 50 mVs^{-1}. "The absence of nanoparticles" indicates that the nanoparticles are neither present on the working electrode nor in the liquid carrier medium. "Otherwise the conditions being the same as the method" indicates that, for example, the working and counter electrodes, any reference electrodes, the liquid carrier medium, and its content of metal ions and counter ions, and the temperature and pressure are the same as in the method.

Preferably, the potential applied to the working electrode has a value at least 0.02 V more positive than the potential at which the deposition of the elemental metal occurs on the working electrode in the absence of the nanoparticles, but otherwise the conditions being the same as the method. Preferably, the potential applied to the working electrode has a value at least 0.05 V more positive than, optionally at least 0.08 V more positive than, optionally at least 0.1 V more positive than, optionally at least 0.2 V more positive than, optionally at least 0.3 V more positive than, optionally at least 0.4 V more positive than, the potential at which the deposition of the elemental metal occurs on the working electrode in the absence of the nanoparticles, but otherwise the conditions being the same as the method.

Preferably, in step (i), the nanoparticles are dispersed in the liquid carrier medium and, in step (ii), the potential applied to the working electrode is (a) less than the underpotential at which deposition of the elemental metal occurs onto the nanoparticles when adsorbed onto the surface of the electrode and are absent from the liquid carrier medium, but otherwise the conditions being the same as the method.

The potential applied to the working electrode preferably has a value less positive than the underpotential for the deposition of the elemental metal onto the surface of the nanoparticle. The potential applied to the working electrode preferably has a value of at least 0.02V less positive than the underpotential for the deposition of the elemental metal onto the surface of the nanoparticle. The potential applied to the working electrode preferably has a value of at least 0.04V less positive, optionally a value of at least 0.08 V less positive, a value of at least 0.1 V less positive, a value of at least 0.2 V less positive, a value of at least 0.3 V less positive, a value of at least 0.4 V less positive, than the underpotential for the deposition of the elemental metal onto the surface of the nanoparticle.

Preferably, in step (i) the nanoparticles are dispersed in the liquid carrier medium and the potential applied to the working electrode in step (ii) is (a) less than the underpotential at which deposition of the elemental metal occurs onto the nanoparticles when adsorbed onto the surface of the electrode and are absent from the liquid carrier medium, but otherwise the conditions being the same as the method and (b) more than the potential at which the deposition of the elemental metal occurs on the working electrode in the absence of the nanoparticles, but otherwise the conditions being the same as the method. The amount of nanoparticles adsorbed onto the electrode can be any amount, since it is the nature of the material of the nanoparticles, not the amount, that will affect the underpotential as described above.

The underpotential of the deposition of the elemental metal onto the nanoparticles from the metal ions in the liquid carrier medium can be determined using any known technique, for example cyclic voltametry. This may be determined, for example, by adsorbing the nanoparticles onto the electrode and placing it in the liquid carrier medium containing the metal ions (but not the nanoparticles), and carrying out a cyclic voltametry experiment by sweeping the voltage between set points either side of the standard electrode potential for the deposition of the metal from the metal ions in the solution onto the electrode; on sweeping from the most positive potential to the most

negative potential, it is possible to identify the underpotential at which deposition of the metal from the metal ions occurs on the working electrode on which the nanoparticles are adsorbed; this may be indicated by a small minimum (sometimes termed a shoulder) on right-hand side of the largest peak on the sweep from the most positive potential to most negative potential. For example, in the Examples of the deposition of cadmium onto silver nanoparticles using a glassy carbon working electrode, the underpotential at which deposition of the cadmium from the cadmium ions occurs onto the working electrode having the silver nanoparticles adsorbed thereon, was determined to be -0.46 V (vs Ag/AgCl). Alternatively, the underpotential of the deposition of the elemental metal onto the nanoparticles may be determined by measuring the most positive potential at which collisions of the nanoparticles are observed using a potentiostat; i.e. the most positive potential at which spikes are observed, indicating charge transfer is occurring during collisions. The potential at which the deposition of the elemental metal occurs on the working electrode in the absence of the nanoparticles can be determined in the same manner (as the underpotential at which deposition of the elemental metal occurs onto the nanoparticles when adsorbed onto the surface of the electrode), and under the same conditions, i.e. the nature and concentration of the metal ions in solution is the same, except that the electrode is free from adsorbed nanoparticles. In the Examples of the deposition of cadmium onto silver nanoparticles using the glassy carbon working electrode, the potential at which deposition of the cadmium from the cadmium ions occurs on the bare glassy carbon working electrode (i.e. free from adsorbed silver nanoparticles), was determined to be -0.82 V (vs Ag/AgCl), as indicated by the single cathodic deposition peak in the sweep from the most positive potential to the most negative potential. Any sweeping in the cyclic voltametery measurements mentioned above should be carried out at a scan rate of 100 mVs^{-1} or less, e.g. 50 mVs^{-1}.

In an embodiment, the potential applied to the working electrode is +/- 0.05 V, preferably +/- 0.025 V, of the potential at which the peak of maximum current is determined by adsorbing the nanoparticles onto the working electrode and placing it in the liquid carrier medium containing the metal ions (but not the nanoparticles), and carrying out a cyclic voltametry experiment by sweeping the voltage between set points either side of the standard electrode potential for the deposition of the metal from the metal ions in the solution onto the electrode; on sweeping from the most positive potential to the most negative potential, the peak of maximum current can be identified; the conditions in the cyclic voltametry, apart from the absence of nanoparticles in the

liquid carrier medium, being the same as in the method. In the Examples, for the deposition of cadmium onto silver nanoparticles using the glassy carbon working electrode on which the nanoparticles are adsorbed, the peak of maximum current was determined to be - 0.75 V. In an embodiment, the potential applied to the working electrode is at or more than the potential at which the peak of maximum current is determined by adsorbing the nanoparticles onto the working electrode and placing it in the liquid carrier medium containing the metal ions (but not the nanoparticles), and carrying out a cyclic voltametry experiment by sweeping the voltage between set points either side of the standard electrode potential for the deposition of the metal from the metal ions in the solution onto the electrode; on sweeping from the most positive potential to the most negative potential, the peak of maximum current can be identified; the conditions during the cyclic voltametry, apart from the absence of nanoparticles in the liquid carrier medium, being the same as in the method. In the above, +/- 0.05 V of a potential X indicates that the potential is in the range of from X-0.05 V to X+0.05 V.

In an embodiment, the nanoparticles comprise silver, the metal of the metal ions in the liquid carrier medium is cadmium, and the method is carried out such that the potential at the working electrode in step (ii) is from about - 0.47 V to about - 0.75 V.

Preferably, the liquid carrier medium is agitated during step (ii). This may be, for example, by passing a gas, for example an inert gas such as nitrogen, through the liquid carrier medium, preferably such that the gas passes near to and optionally contacts the working electrode. In alternative embodiments, the liquid carrier medium may be induced to flow past the working electrode.

A plurality of atomic layers of the elemental metal are coated onto the nanoparticles. Optionally, at least 5 atomic layers of the elemental metal are coated onto the nanoparticles. Optionally, at least 10 atomic layers of the elemental metal are coated onto the nanoparticles. Optionally, at least 15 atomic layers of the elemental metal are coated onto the nanoparticles.

The number of atomic layers deposited can be calculated by determining the amount of charge transferred to a nanoparticle during a collision with the electrode, by which method the number of electrons transferred can be calculated. The amount of charge transferred per collision can be determined by plotting the current against time and integrating the period during a collision of a nanoparticle with an electrode (generally

shown by a spike). The surface area for a nanoparticle can also be calculated. From this, a monolayer coverage of the metal to be deposited, in terms of the number of atoms of this metal, can also be calculated. For example, as is illustrated in the Examples, a monolayer coverage of cadmium on a silver nanoparticle with fcc geometry used in the Examples was calculated to be 10^5 atoms cadmium. Such calculations can be applied to other nanoparticles and metals to be deposited by analogy.

Preferably, the conditions of the method are adapted such that, for at least some collisions, at least 1×10^{-12} C is transferred per collision, optionally at least 1×10^{-11} C is transferred per collision, optionally at least 1×10^{-10} C is transferred per collision, optionally at least 2×10^{-10} C is transferred per collision, optionally at least 3×10^{-10} C is transferred per collision, optionally at least 4×10^{-10} C is transferred per collision, optionally at least 5×10^{-10} C is transferred per collision, optionally at least 1×10^{-9} C is transferred per collision, optionally at least 1×10^{-8} C is transferred per collision. The collisions can be observed using a potentiostat, and, as mentioned above, the amount of charge transferred per collision can be determined by plotting the current against time and integrating the period during a collision of a nanoparticle with an electrode (generally shown by a spike).

Preferably, the conditions of the method are adapted such that, for at least some collisions, at least 1×10^4 atoms of the metal are deposited from the metal ions in the liquid carrier medium per collision, preferably at least 1×10^5 atoms of the metal are deposited from the metal ions in the liquid carrier medium per collision, preferably at least 5×10^5 atoms of metal are deposited from the metal ions in the liquid carrier medium per collision, preferably at least 1×10^6 atoms of the metal are deposited from the metal ions in the liquid carrier medium per collision, preferably at least 2×10^6 atoms of the metal are deposited from the metal ions in the liquid carrier medium per the liquid carrier medium per collision, preferably at least 4×10^6 atoms of the metal are deposited from the metal ions in the liquid carrier medium per collision.

The method may be carried out at any suitable temperature and pressure. Optionally, the method is carried out at a temperature of from 0 °C to 50 °C, optionally from 10 °C to 30 °C. Optionally, the method is carried out at a pressure of from 90 kPa to 110 kPa, optionally from 95 KPa to 105 kPa, optionally from 98 kPa to 102 kPa.

As mentioned above, in a fourth aspect, the present invention provides a nanoparticle having a core comprising a first elemental metal and an electrochemically-deposited coating of a second elemental metal on the core, wherein the coating is in the form of a bulk deposit of the second elemental metal. The nanoparticle of the fourth aspect may be producible in accordance with the method of the first aspect. The first elemental metal may be the first metal as described above and the second elemental metal may be the second metal described above. The core of the nanoparticle may be as described above for the nanoparticles, in step (i) of the method.

Embodiments of the present invention will now be described with reference to the following non-limiting Examples and the accompanying drawings.

Examples

Silver Nanoparticles (AgNPs) were synthesized according to the method of Pyatenko *et al.* [1-3] and characterized by SEM imaging to have a mean radius of 45 nm, with the standard deviation being 3 nm (the mean radius is a number average over 300 or more nanoparticles in an SEM image of them; and the standard deviation is calculated as known in the art). AgNPs were dispersed by ultrasound prior to their addition to the solution. An aliquot of AgNPs was determined to give a particle density of 9×10^{12} particles dm^{-3} in the volume of electrolyte used in the reaction cell. In more detail, the particle density was determined as follows:

1. A sample of AgNPs suspended in solution was dispersed and an aliquot (in this case 20 μL) deposited onto a clean, dry glassy carbon (GC) electrode (of radius typically 1-3mm). The solvent was then allowed to evaporate.
2. The AgNP-modified GC electrode was placed into an electrochemical cell containing a suitable counter and reference electrode and electrolyte solution. An oxidative scan was then run, and the stripping voltammogram of the AgNPs being exhaustively oxidised from the surface into Ag^+ ions recorded.
3. By integration of the stripping peak, the number of Ag atoms present on the GC electrode surface was determined using Faraday's Law. Knowing the approximate mean NP size and density of Ag, the number of atoms of Ag was converted into a number of AgNPs. This provided the number of AgNPs in the original aliquot of 20μL, from which the density in a dm^3 can be calculated.

Cadmium chloride and sodium chloride (Aldrich, >99%) were used as received. Deposition solutions were made of 1 mM $CdCl_2$ and 0.10 NaCl, using ultrapure water of resistivity ≥ 18.2MΩ.cm (Millipore) and degassed thoroughly with N_2 (oxygen free, BOC Gases plc) and an atmosphere of N_2 maintained during the experiment. Experiments were conducted within a faraday cage using a μAutolab III potentiostat with a time resolution shorter than 0.1 ms (Metrohm-Autolab BV, Utrecht, Netherlands) and a three-electrode arrangement: an 11μm radius glassy carbon (GC) working electrode (BASi Inc), a graphite counter electrode, and a Ag/AgCl reference electrode (Radiometer, Copenhagen). Impact spikes were analysed using Origin v.8.1 for spike identification and integration, and electrical noise reduction [4].

Examples 1 and 2

The voltammetry of cadmium deposition was recorded at a scan rate of 50 mV s^{-1} on a bare GC electrode (of diameter 3mm) - Example 1 - and the same GC electrode covered with immobilised AgNPs [5-8] - Example 2 - both immersed in a 1 mM solution of $CdCl_2$ (aq) and 0.10 M NaCl. The resulting voltammogram is shown in Figure 1. In the case of the bare GC electrode, a single cathodic deposition peak was observed at -0.82V (vs Ag/AgCl), whereas in the case of the AgNP-modified GC electrode the same peak was observed at -0.75 V, along with a cathodic UPD feature at -0.46 V. These results were in good agreement with Campbell and Compton [9]. It was noted that the significant reductive features reported for the desorption and discharge of chloride ions on Ag(111) [10] were not apparent under the experimental conditions and did not present interference with the UPD peak.

Figure 1 shows Cadmium deposition on a bare GC electrode (dotted lines, Example 1) and a AgNP-modified GC electrode (solid lines, Example 2): (a) shows full voltammograms, whilst (b) shows only the underpotential deposition region.

Examples 3 and 4

A GC microelectrode (of radius 11 μm) was then placed in a degassed solution of 1 mM $CdCl_2$ and 0.1M KCl and the potential held at -0.55V (the potential where underpotential deposition is found to occur). An aliquot of dispersed AgNPs was then added to the solution, which was then agitated by bubbling with N_2. The result is Example 3. Impact transients were recorded for Example 3 and these are shown in Figure 2. The impact transients were observed as sharp, reductive spikes of duration 1-10 ms and peak heights of several nA, similar to those previously recorded for nanoparticle impact events [4,11-13]. Over one hundred impact spikes were recorded and analysed according to the procedure published in Zhou *et al.* [4]. The frequency of collisions was consistent with previous measurements of *ca.* 1.8 collisions s^{-1} at this size electrode with the same concentration of nanoparticles (9×10^{12} particles dm^{-3}). No spikes were found to occur when the electrode was potentiostatted at potentials more positive than the UPD feature (for example at -0.30V) [Example 4], confirming that the reductive transients were due to the deposition cadmium on the AgNPs during the collisions with the GC electrode surface:

$$Cd^{2+}(aq) + 2e^- \rightarrow Cd(np)$$

Analysis of the spikes according to a previously described method [13], enabled the charge passed per impact spike to be converted into an approximate coverage of an average single nanoparticle, since the charge passed per impact transient, Q, is related to the number of electrons passed, *N*, via the electronic charge according to

$$Q = eN \qquad (1)$$

and a surface area (*S*) can be calculated for a single, fcc geometry AgNP with knowledge of the Ag atomic radius, r_A.

$$S = 24 r_A^2 N^{2/3} \qquad (2)$$

This therefore allows monolayer coverage of Cd atoms (θ= 1) to be calculated to be 9.1 $\times$ 10^5 atoms for a mean AgNP. Figure 2 shows that, in the case of Cd UPD, the agreement of the experimental data to approximately monolayer coverage is very good: at these ionic strengths, agglomeration of AgNPs is rapid to the point where after 20mins, less than 20% of the AgNP species present are in the form of single dispersed nanoparticles, the remainder being larger cluster species [11]. The most common clusters observed in Rees *et al.* [11] were of 4 and 8 nanoparticles, which have surface areas of 3 and 4 times greater than the single NP used as the basis for the scale in Figure 2.

Figure 2, therefore, shows a) a typical impact transient at -0.55V, and b) a histogram showing the number of impacts in terms of layer coverage of an average AgNP. The present inventors consider that the appearance of particles having an apparent coverage of θ greater than 1 is in fact the monolayer or sub-monolayer coverage of clusters of AgNPs. This is in agreement with the findings in the paper by Zhou et al entitled Nanoparticle-Electrode Collision Processes: The Underpotential deposition of Thallium on Silver Nanoparticles in Aqueous Solution (ChemPhysChem). In this paper, as shown in Figure 5, again there was an apparent coverage of θ greater than 1, but this has been attributed to monolayer, or sub-monolayer, coverage of clusters of silver nanoparticles; in otherwords, not a bulk deposition of thallium on the nanoparticles.

Examples 5 and 6

The bulk deposition of cadmium onto AgNPs was investigated by verifying the deposition of Cd onto a bare GC electrode. The GC microelectrode was placed in a degassed solution of 1mM $CdCl_2$ and 0.10 M NaCl, the potential held at -0.74 V for 5 seconds and then smoothly swept back to +0.5V at a scan rate of 20mV s^{-1} in order to observe the anodic stripping of any deposited metals [Example 5]. As shown in Figure 3, no direct deposition of Cd onto the GC electrode was observed (Figure 1 indicates that the Cd stripping peak commenced at -0.70V).

Figure 3, therefore, shows a) a potential step-sweep experiment of a GC electrode (of radius 11µm) in 1mM $CdCl_2$ and 0.10M NaCl (Example 5). The potential was held at -0.74V (vs Ag/AgCl) and scanned positive at 20 mV s^{-1}. (b) shows an enlargement of the "transient" region after noise reduction to confirm no spikes.

The addition of aliquots of AgNPs under the same conditions (Example 6) as for Example 5 resulted in numerous reductive collision spikes being recorded: these are illustrated in Figure 4. These spikes were considerably larger than those observed for UPD processes and were of the order of 10^{-12} C per spike. In this case, Cd has clearly been deposited, due to the clear cadmium stripping peak observed in the anodic sweep. The charge passed under the Cd stripping peak was found to be *ca.* 6.5×10^{-10} C (an average of 5 experiments): 6-60 times greater than the total charge passed under the impact spikes, leading to the conclusion that at -0.74V the majority of the Cd bulk deposition occurs at adsorbed AgNPs. Analysis of the Ag stripping peak at +0.05V indicated that an average of 5.2×10^{-10} C charge is passed, corresponding to *ca.* 168 single AgNPs.

Figure 4 (Example 6) shows similar information to Figure 3 (Example 5), except that 9×10^{12} particles dm^{-3} of AgNPs is also present. (b) shows an enlargement of the "transient" region post-noise reduction.

Example 7

An experiment almost identical to that in Example 6 was performed, but at a potential of -0.73V: this is Example 7. A "step-sweep" plot is set forth in Figure 5. At this potential, no discernible Cd stripping feature was observed when in the presence of AgNPs despite there being significant deposition impact spikes (average charge = 4.4 $\times$ 10^{-10} C). The frequency of collisions is consistent with previous measurements of *ca.* 1.8 collisions s^{-1} at this size of electrode, with the same concentration of nanoparticles (9×10^{12} particles dm^{-3}). We speculate that there is in fact some Cd deposition on the adsorbed AgNPs (formed by sticking collisions between the NPs and the electrode), but that the stripping feature is too small and broad due to surface alloying [10,14,15] to be reliably measured above the baseline.

Figure 5 shows (a) a potential step-sweep experiment of a GC electrode (of radius 11μm) in 1mM $CdCl_2$ and 0.10M NaCl (Example 7). The potential was held at -0.73V (vs Ag/AgCl) and scanned positive at 20 mV s^{-1} - no Cd stripping feature was observed; and (b) an enlargement of the "transient" region after noise reduction showing spikes.

Analysis of the deposition spikes at -0.73V yielded a distribution of charges passed per impact, which can be converted into an approximate coverage of an average single nanoparticle using Equations 1 and 2 (as described above).

Figure 6 is a histogram showing the number of impacts in terms of layer coverage of an average AgNP. It sets forth the distribution of NP coverages confirming that multilayers of Cd are deposited onto the AgNPs during collision, i.e. a bulk deposit of Cd on the nanoparticles.

We therefore conclude that for the first time, electroplating has been demonstrated to occur at nanoparticles during their collisions with an inert electrode, in this case the bulk deposition of Cd onto AgNPs:

$$Cd^{2+}(aq) + 2e^{-} \rightarrow Cd(np)$$

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Each of the above references is incorporated herein by reference in its entirety.

CLAIMS

1. A method of electrochemically coating nanoparticles, the method comprising:

(i) providing a working electrode, a counter electrode, and a liquid carrier medium in contact with the working electrode, the liquid carrier medium comprising:

(a) the nanoparticles, wherein the nanoparticles comprise a first material;

(b) ions of a metal dissolved in the liquid carrier medium;

(ii) applying a potential between the working electrode and the counter electrode, such that, at the working electrode, the ions of the metal are reduced and there is a bulk deposition of the elemental metal onto the nanoparticles.

2. The method according to claim 1, wherein the first material is or comprises a first metal, which is in elemental form, and the metal of the ions in solution is a second metal, the first and second metal are different to one another.

3. The method according to claim 2, wherein the first metal and second metal are different transition metals.

4. The method according to any one of the preceding claims, wherein the first material comprises silver, and the metal of the ions in solution is a transition metal other than silver.

5. The method according to claim 4, wherein the metal of the ions in solution is cadmium.

6. The method according to any one of the preceding claims, wherein the diameter of at least some of the nanoparticles, in step (i), is from 1 nm to 100 nm.

7. The method according to any one of the preceding claims, wherein at least 5 atomic layers of the elemental metal are coated onto the nanoparticles.

8. The method according to any one of the preceding claims, wherein the nanoparticles are dispersed in the liquid carrier medium and the potential applied to the

working electrode is less than the underpotential for the deposition of the elemental metal onto the surface of the nanoparticle.

9. The method according to any one of the preceding claims, wherein, in step (i), the nanoparticles are dispersed in the liquid carrier medium and, in step (ii), the potential applied to the working electrode is (a) less than the underpotential at which deposition of the elemental metal occurs onto the nanoparticles when adsorbed onto the surface of the electrode and are absent from the liquid carrier medium, but otherwise the conditions being the same as the method and (b) more than the potential at which the deposition of the elemental metal occurs on the working electrode in the absence of the nanoparticles, but otherwise the conditions being the same as the method.

10. The method according to any one of the preceding claims, wherein the nanoparticles in step (i) comprise silver in elemental form, the metal of the metal ions in the liquid carrier medium is cadmium, and the method is carried out such that the potential at the working electrode in step (ii) is from about - 0.47 V to about - 0. 75 V.

11. The method according to any one of the preceding claims, wherein both the working electrode and the counter electrode are carbon-containing electrodes.

12. A coated nanoparticle producible according to the method of any one of claims 1 to 11.

13. A nanoparticle having a core comprising a first elemental metal and an electrochemically-deposited coating of a second elemental metal on the core, wherein the coating is in the form of a bulk deposit of the second elemental metal.

14. A nanoparticle according to claim 13, wherein the first and second elemental metals are different transition metals.

15. A nanoparticle according to claim 14, wherein the first elemental metal is silver and the second elemental metal is cadmium.

16. An apparatus for carrying out the method according to any one of claims 1 to 11, the apparatus comprising:

a working electrode and a counter electrode, and a liquid carrier medium in contact with the working electrode, the liquid carrier medium comprising:

(a) the nanoparticles, wherein the nanoparticles comprise a first material;

(b) ions of a metal dissolved in the liquid carrier medium;

wherein a potential between the working electrode and the counter electrode can be applied, such that, at the working electrode, the ions of the metal can be reduced and there is a bulk deposition of the elemental metal onto the nanoparticles.

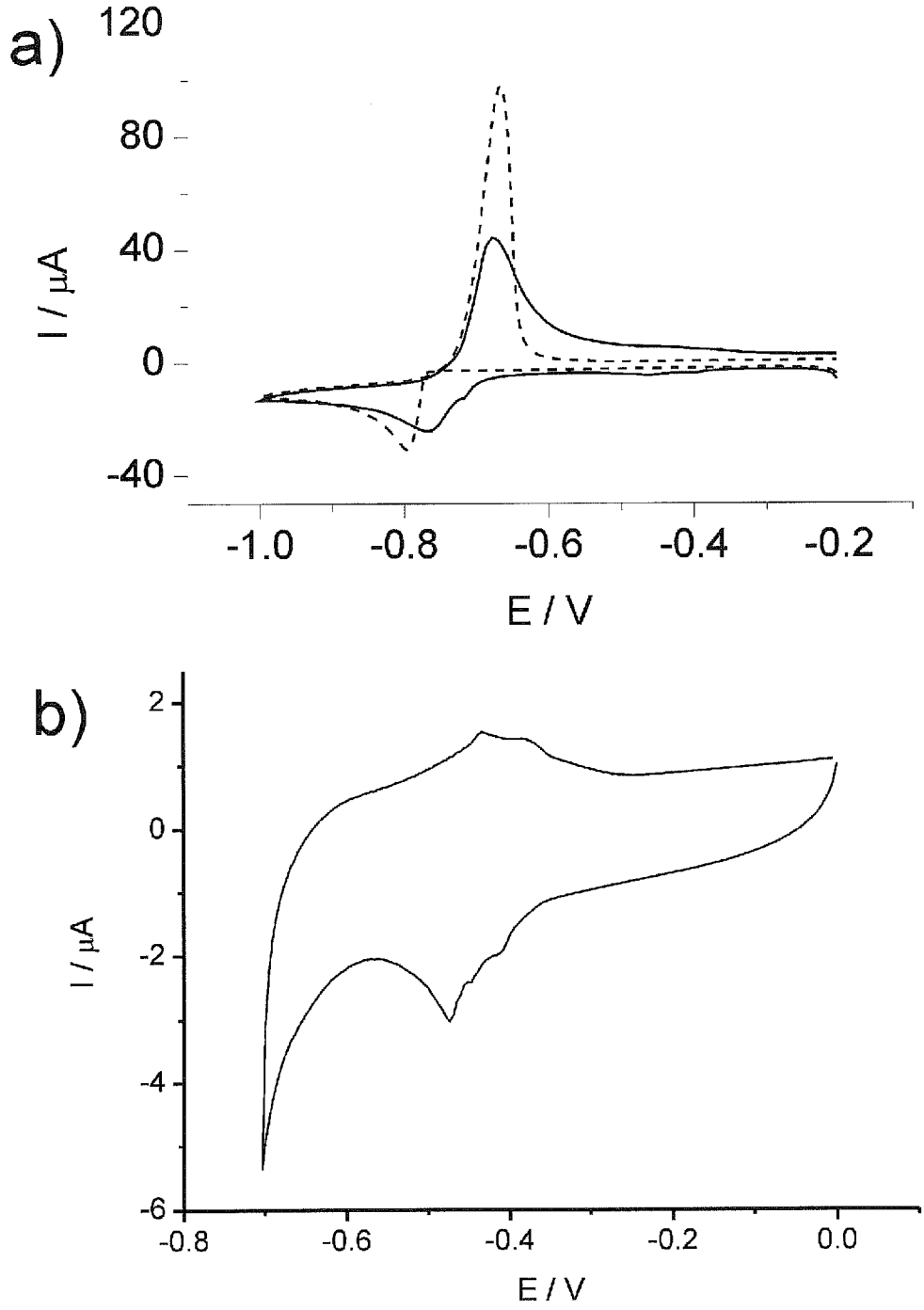

Fig. 1

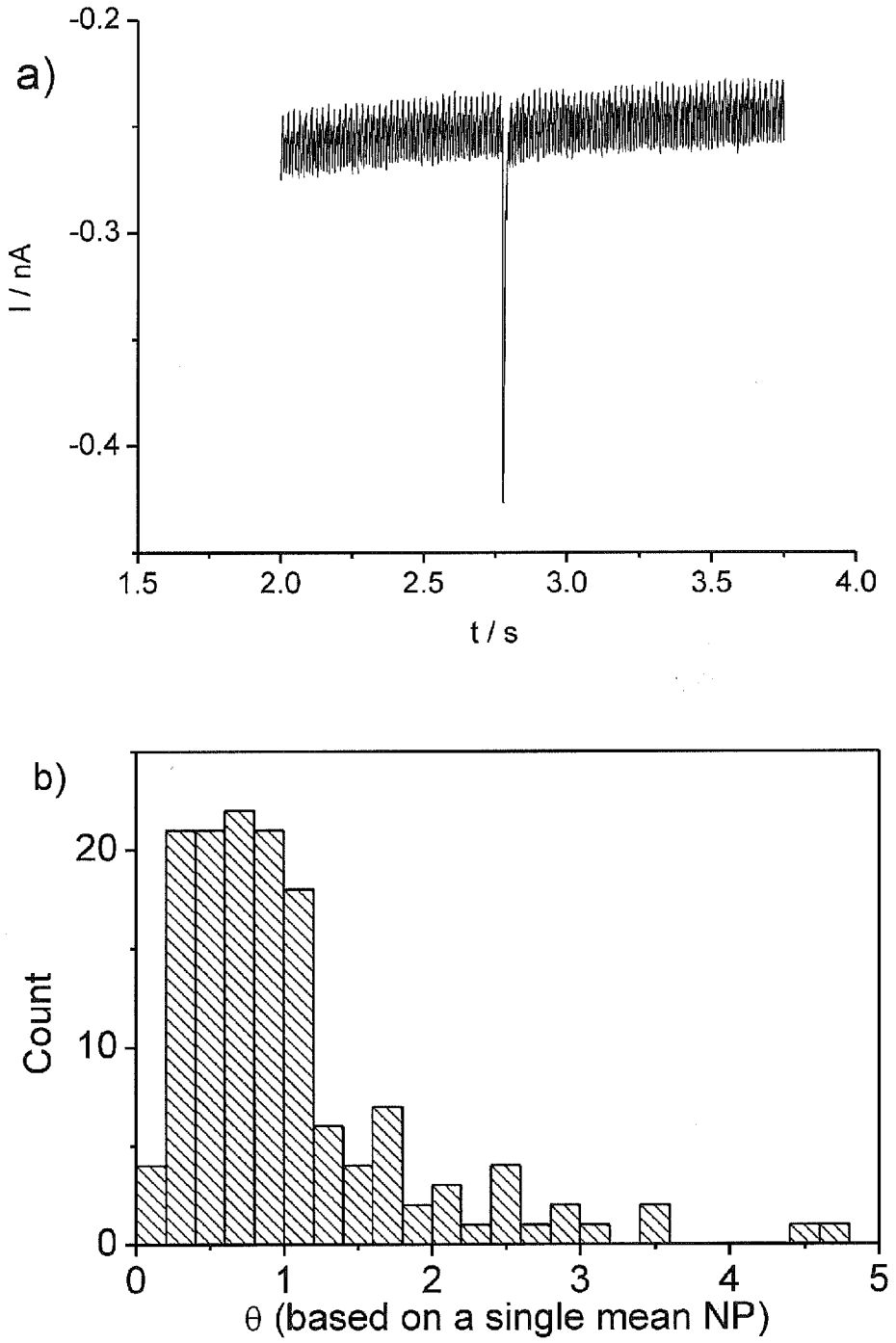
a)
-0.2
-0.3
-0.4
I / nA
1.5
2.0
2.5
3.0
3.5
4.0
t / s
b)
20
10
0
Count
0
1
2
3
4
5
θ (based on a single mean NP)

Fig. 2

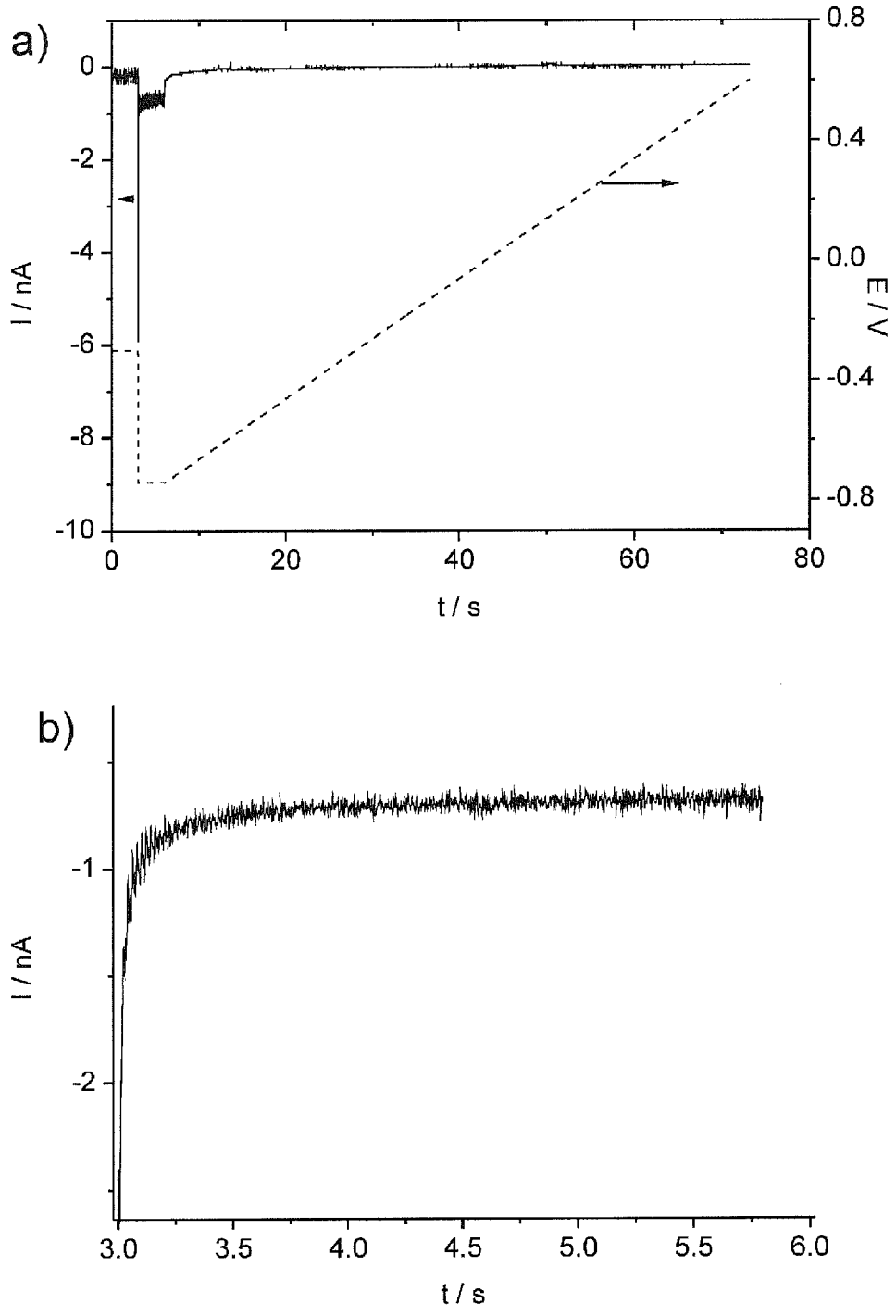
a)
0
-2
-4
-6
-8
-10
I / nA
0.8
0.4
0.0
-0.4
-0.8
E / V
0
20
40
60
80
t / s
b)
-1
-2
I / nA
3.0
3.5
4.0
4.5
5.0
5.5
6.0
t / s

Fig. 3

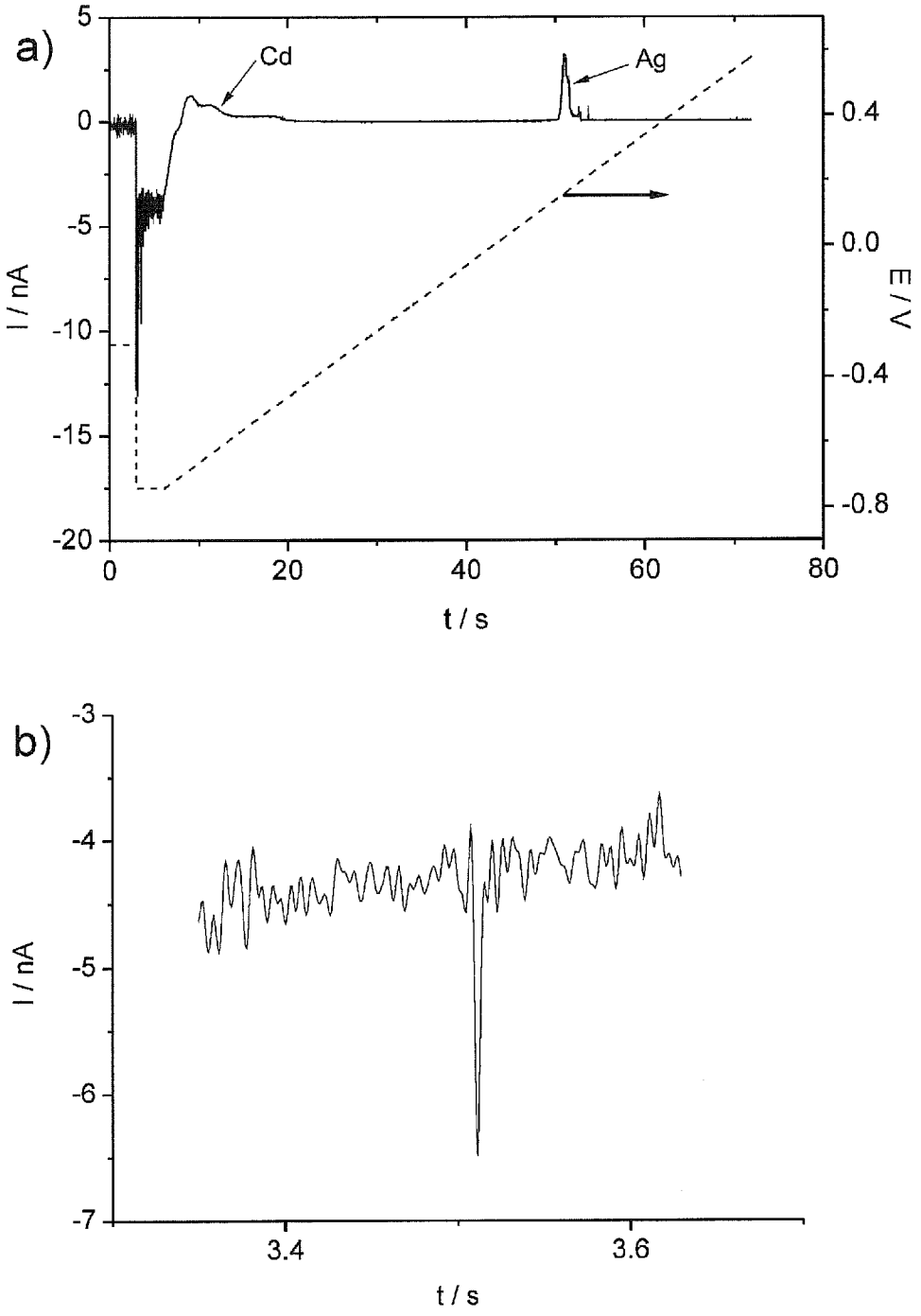

Fig. 4

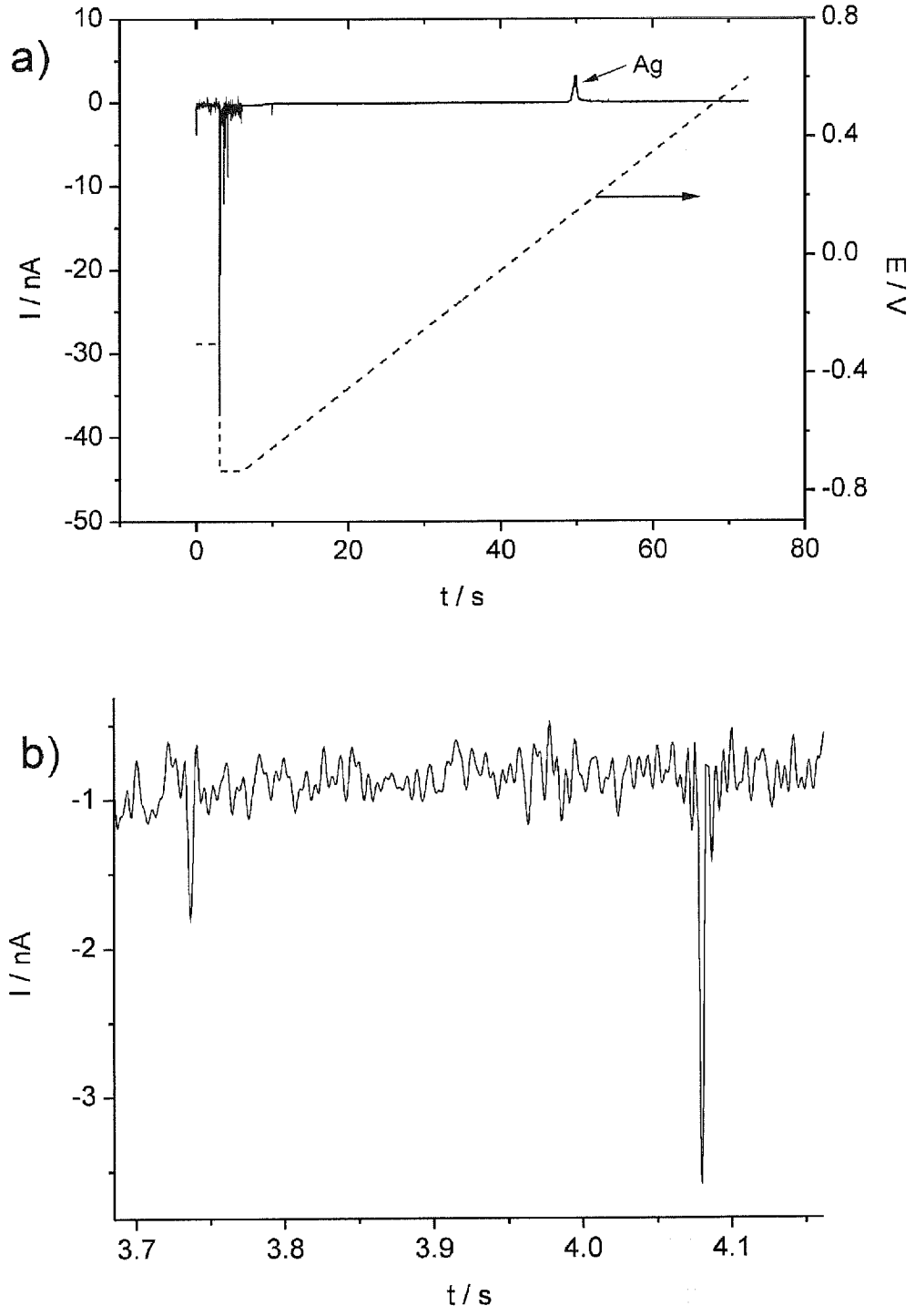
a)
Ag
I / nA
E / V
t / s
10
0
-10
-20
-30
-40
-50
0.8
0.4
0.0
-0.4
-0.8
0
20
40
60
80
b)
I / nA
t / s
-1
-2
-3
3.7
3.8
3.9
4.0
4.1

Fig. 5

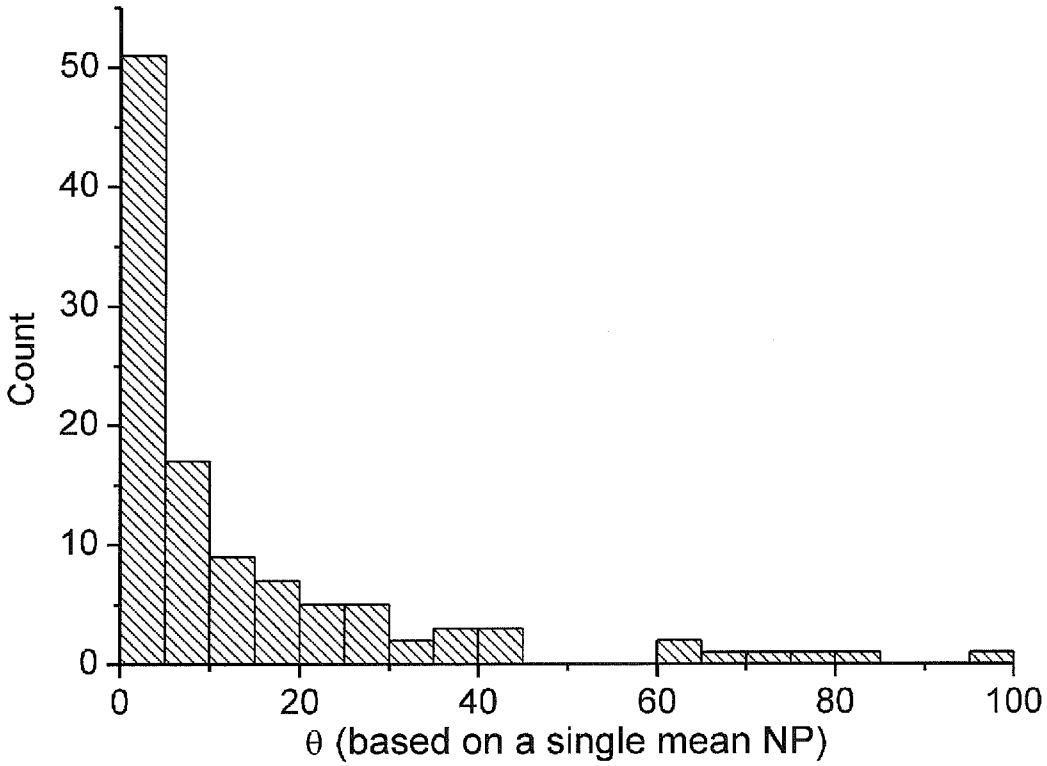

Fig. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/051466

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F1/00 B22F1/02 C25C5/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22F C25C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YI-GE ZHOU ET AL: "Nanoparticleelectrode collision processes: The electroplating of bulk cadmium on impacting silver nanoparticles", CHEMICAL PHYSICS LETTERS, vol. 511, no. 4, 12 June 2011 (2011-06-12) , pages 183-186, XP028247597, ISSN: 0009-2614, DOI: 10.1016/J.CPLETT.2011.06.015 [retrieved on 2011-06-12] Experimental Section Results and discussion	1-16

X	US 2009/178933 A1 (ZENG TAOFANG [US]) 16 July 2009 (2009-07-16)	1-4,6, 12-14,16
A	examples claims 1,3	5,7-11, 15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 September 2012	26/09/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Morra, Valentina

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2012/051466

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009178933 A1	16-07-2009	CN 101952197 A	19-01-2011
		US 2009178933 A1	16-07-2009
		WO 2009126341 A2	15-10-2009